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METAL-OXIDANT IGNITER MATERIALS

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JAN 15 1973

ABSTRACT

An investigation of the physical and chemical factors affecting propellant ignition is being conducted with the ultimate objective of producing information useful in the design and development of ignition systems for solid-propellant rockets. This investigation has largely been concerned with a study of the materials used to ignite rocket motors, that is, black powder and metal-oxidant formulations. This paper presents the results of calculations made on five metal fuels with conventional oxidizers to determine, under adiabatic conditions, what maximum flame temperatures could be reached and what the physical states of the products might be. Results of experimental characterization studies covered in this paper include determinations of heats of explosion, gas volumes produced, and the effectiveness of various igniter compositions in igniting a propellant specimen in a laboratory ignitibility test. In addition, unusual ignitibility effectiveness of fuel-rich magnesium—potassium nitrate mixtures is discussed in terms of a secondary ignition effect of igniter combustion products, and the results of a limited investigation of factors affecting the combustion rate of elemental boron are given.

INTRODUCTION

The use of metal-oxidant materials to ignite solid-propellant rockets has become an accepted procedure where black powder or resin-oxidizer compositions are either inadequate to transfer ignition to a propellant grain satisfactorily or produce undesirable pressure peaks in the process. Because of the high heats of combustion of the metallic components and thermal stability of the oxides formed, metal-oxidant igniters develop high flame temperatures. In addition to the usual modes of heat transfer to the propellant afforded by black powder, namely, convection and radiation, the metal-fuel igniter may efficiently transfer heat by (1) condensation of vapors on the surface liberating the heats of vaporization and fusion, (2) impingement of solid particles on the surface, and (3) improved radiation due to high emissivity of the particles. By using these more powerful modes of heat transfer and by

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2. The attached technical paper, "Metal-Oxidant Igniter Materials," by
Samuel Zeman, is included in the 2nd JANNAF Ignition Symposium, Volume I,
1956, which is not available at this Command. It is suggested that a
copy of the entire symposium be obtained from the Chemical Propulsion
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as

       F. W. JAMES
       Director, Propulsion Directorate
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       and Engineering Laboratory

...propria...ly varying the composition of the igniter, it is possible to ...ect much better control over the heat-transfer rate tha: is possible ...th black powder alone.

In this paper, estimates are given of the maximum fl... ...mperatures that can be reached by various binary metal-oxidan. ...xtures under adiabatic conditions, and the experimental performance ...aracteristics of many of these compositions in small-scale tests have been determined.

ADIABATIC FLAME TEMPERATURE CALCULATIONS

The maximum flame tem.erature of an igniter reaction serves partly to indicate the rate of heat transfer from the igniter products to the propellant, a factor of importance in determining propellant ignition effectiveness of various metal-oxidant mixtures. It is true that the attainment of high temperatures is a necessary function of igniters, but practical considerations in many cases limit the design of igniter compositions and configurations to temperature levels consistent with propellant and rocket syste.. requirements. In such cases the attainment of maximum flame temperatures that might give rise to ...ssu.: ...eaks a. a ...o... transients is undesirable, and of greater ...ortanc.. .. ...re e...c...... ...ili.ation of igniter combustion products transferri..., heat to the prop. ..ant surface. The evolution of metallic oxides having nigh latent heats o. ...sion and vapori.ation and .. ... heat capacities at relatively high temp..ratures is .. many ca.es mo.. desirable in ignition than achievement of high flame temperatures. Nevertheless, it is of interest to know the limiting va...es of adiabatic flame temperatures produced by various metal-oxidant mixtures.

The chemical reactions chosen for the production of hig.. temperatures must fulfill several simultaneous requirements: ..) the reaction must be rapid, (2) the reaction must produce a high ...othermic heat of reaction, (3) the products must have great thermal ...bility, and (4) the heat capacities of the products should be low. ..e re... .ements of ra... .reaction and high exothermicity, although ...ortant, are generally recognized, whereas the importance of ...rmal stability is frequently overlooked. The role played by ...ssociation of the reaction products in limiting attainment of very ...gh temperatures can be illustrated by the combustion of carbon in ..ygen. The theoretical temperature attainable in this case is about ...0,000°C. Actually, however, owing to the dissociation of the reaction products, 2500°C represents about the maximum possible temperature

attainable in this combustion. These same considerations apply in the combustion of metals and emphasize the importance of reaction product stability in producing high temperatures. Indeed, the high temperatures capable of being produced by the combustion of metals is due, for the most part, to the high thermal stability of certain metallic oxides.[1]

Whereas the adiabatic flame temperatures of propellants may be accurately calculated, similar calculations for inorganic explosives or pyrotechnics yield results that can only be accepted as approximation of the true values. This is because parameters such as heats of reaction, mechanism and extent of reaction, heat capacities at high temperatures of the products, the nature and energies involved in phase transitions, and dissociation of the various products are not accurately known.

The method used for calculating maximum flame temperatures of 15 igniter reactions in this paper is similar to that used by Levy[2] for several primer mixtures, but the calculations include corrections for dissociation of certain products because of the high temperatures involved. To carry out the required calculations, it was necessary to extrapolate the available specific-heat data to very high temperatures, to use data for analogous compounds in a few instances, and to make logical estimates of phase-transition heats and heat capacities in several cases.

The flame temperatures were first calculated assuming no dissociation of the products. The temperatures calculated by this method were all very high, and subsequent calculations were made including corrections for dissociation. The calculations are based on the igniter mixtures reacting instantaneously at 300°K according to the assumed mechanisms and the resulting products then being heated to the adiabatic flame temperature. To estimate the flame temperature, the heat contents of the products of reaction plus the heat absorbed in phase changes were set equal to the heat of reaction, namely

$$\Delta H_1 = \left[\int^{T_M} C_{p_s}\, dt + \Delta H_f + \int_{T_M}^{T_V} C_{p_l}\, dt + \Delta H_v + \int_{T_V}^{T_F} C_{p_g}\, dt + \Delta H_d \right]_A$$

$$+ \left[\qquad \right]_B + \left[\qquad \right]_C + \ldots$$

where ΔH_1 = heat of reaction at 298°K

T_M = melting point of each product

T_V = boiling point of each product

T_F = flame temperature

C_{p_s}, C_{p_l}, C_{p_g} = molar heat capacities of each product in solid, liquid, and gaseous states, respectively

ΔH_f, ΔH_v, ΔH_d = heats of fusion, vaporization, and dissociation, respectively

A, B, C, etc. = individual reaction products

The reactions were assumed to proceed in the following manner, the extent of reaction being dependent on temperature and quantity of energy available:

$$KClO_4(s) \rightarrow KCl(s) \rightarrow KCl(l) \rightarrow KCl(g) \rightarrow K(g) + Cl(g)$$

$$Ba(NO_3)_2(s) \rightarrow BaO(s) \rightarrow BaO(l) \rightarrow BaO(g) \rightarrow Ba(g) + O(g)$$

$$KNO_3(s) \rightarrow K_2O(s) \rightarrow K(g) + O(g)$$

$$Mg(s) \rightarrow MgO(s) \rightarrow MgO(l) \rightarrow MgO(g)$$

$$Al(s) \rightarrow Al_2O_3(s) \rightarrow Al_2O_3(l) \rightarrow AlO(g) + O(g)$$

$$Ti(s) \rightarrow Ti_2O_3(s) \rightarrow Ti_2O_3(l) \rightarrow TiO(g) + TiO_2(g)$$

$$Zr(s) \rightarrow ZrO_2(s) \rightarrow ZrO_2(l) \rightarrow ZrO_2(g)$$

$$B(s) \rightarrow B_2O_3(s) \rightarrow B_2O_3(l) \rightarrow B_2O_3(g) \rightarrow BO(g) + O(g)$$
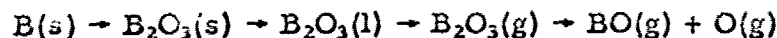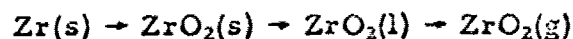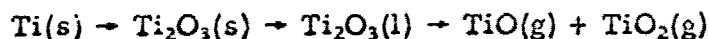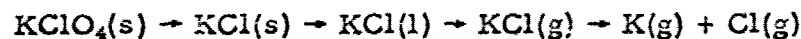
Table I gives the thermochemical constants for the metals, oxidizers, and their reaction products. It is seen from Table I that all the metallic oxides except B_2O_3 have relatively high heats of fusion at high temperatures, which contributes to their effectiveness as heat-transfer media in ignition systems. Heats of vaporization of the metallic oxides are very high, and in all cases except for boron, the maximum flame temperatures that can be attained are limited by the vaporization temperatures. Indications are that ZrO_2, MgO, and B_2O_3

survive the vaporization process as gaseous species, whereas Al_2O_3 and Ti_2O_3 dissociate on vaporization at high temperatures into simpler molecules or atoms.[8, 14-17] Table I indicates that the thermal stability of gaseous oxidizer decomposition products decreases in the order BaO, KCl, K_2O, with K_2O being almost nonexistent as a gas and BaO having the lowest tendency to dissociate.[8, 11, 12, 18]

Table II gives the heat-capacity data for the assumed products of igniter reactions; as can be seen, data for many of these simple compounds at low as well as high temperatures are not available in the literature. As with latent heats of phase changes, the heat capacities of the metallic oxides are high, particularly in the liquid states. It should be noted that B_2O_3, which has a heat of fusion of only 5.5 kcal/mole, may exist as a liquid from 723 to 2500°K, with an average heat capacity of 30.5 cal/mole/°K, and may transfer 54.9 kcal/mole as it cools from its boiling point to the fusion temperature.

The following sample calculation for the reaction between zirconium and potassium perchlorate will illustrate the methods employed in obtaining the results shown in Table III.

Composition:

56.84% Zirconium
43.16% Potassium perchlorate

Reaction: in moles or gram atoms per 100 grams

$$0.6231 Zr(s) + 0.3115 KClO_4(s) \rightarrow 0.6231 ZrO_2(s) + 0.3115 KCl(s)$$

The heat of reaction, in kilocalories per 100 grams, is therefore

H reaction = H products − H reactants

| | ZrO_2 | | KCl | | $KClO_4$ | | Zr |

$$\Delta H_1 = (0.6231)(258.4) + (0.3115)(104.3) - (0.3115)(112.71) - (0.6231)(0)$$

$$\Delta H_1 = 158.39 \text{ kcal/100 grams}$$

With the knowledge that 158.39 kcal is evolved from the reaction, a flame temperature is assumed and a determination is made of the heat required to raise the products to the assumed temperature. The energy required to heat the products to the assumed temperature may then be plotted graphically versus the assumed temperature. By graphically interpolating, the adiabatic flame temperature is found.

However, for the example given when a flame temperature is assumed
of 4600°K, the approximate boiling point of ZrO_2, sufficient energy is
found to be available from the reaction to vaporize only a portion of the
ZrO_2. Moreover, a study of the literature indicates that KCl(g) dis-
sociates at temperatures below 3000°K. A separate calculation is made
to determine the extent of dissociation of KCl(g) into atoms at various
temperatures. The product of heat of dissociation and fraction dis-
sociated is then treated in the same manner as latent heats. The
products of the overall reaction are then represented as absorbing
heat through their various phase changes and by integration of the heat-
capacity equations over the temperature range. The heat absorbed by
dissociation of KCl at the flame temperature is added to the latent heats
and the heat absorption due to heat capacities and again equated graphi-
cally to the heat of reaction, ΔH_1. If this equality is not obtained, a
new temperature higher, or lower, is assumed, and the calculation is
repeated until a heat balance is obtained. In the example given, the
flame temperature is limited by the boiling point of ZrO_2, and after
other assignments have been made, any excess energy available is
shown to be absorbed in vaporizing the proportionate fraction of
$ZrO_2(l)$.

The extent of dissociation of gases such as KCl at high
temperatures was determined by solving for the equilibrium constant,
K, from the relation

$$\log K = \frac{-\Delta F}{2.3RT}$$

The change in free energy, ΔF, for the dissociation reactions was
determined from the derived equation

$$\Delta F = \Delta H_0 - \Delta C_p T 2.3 \log T + [6.7 \Delta C_p - \Delta S_{298}] T$$

for the reaction

where $\Delta H_0 = \Delta H_{298} - 298 \Delta C_p$

$\Delta H_{298} = \Delta H_{298}$ (products) $- \Delta H_{298}$ (reactants)

$\Delta C_p = C_p$ (products) $- C_p$ (reactants)

$\Delta S_{298} = S$ (products) $- S$ (reactants)

(C_p and S are heat capacity and entropy, respectively.)

Using the latent heats and other thermodynamic data from Table I and integration of the heat-capacity equations from Table II, the following equations represent the assignment of heats absorbed in raising the products to the limiting flame temperature, which is 4600°K:

$\Delta H_2 = ZrO_2(s) \rightarrow ZrO_2(l) = (0.6231)(20.8) =$ 12.96 kcal

$\Delta H_3 = KCl(s) \rightarrow KCl(l) = (0.3115)(6.1) =$ 1.90

$\Delta H_4 = KCl(l) \rightarrow KCl(g) = (0.3115)(38.8) =$ 12.09

(It is found by separate calculation that KCl(g) is 74% dissociated at 4600°K.)

$\Delta H_5 = KCl(g) \rightarrow K(g) + Cl(g) = (0.3115)(105)(0.74) =$ 24.20

The following heat-capacity equations show the product of moles, average heat capacity found by integrating equations in Table II, and temperature difference.

$C_1 = ZrO_2(s)(300°-2988°) = (0.6231)(29.13)(2688)(10^{-3}) =$ 48.79

$C_2 = ZrO_2(l)(2988°-4600°) = (0.6231)(35)(1612)(10^{-3}) =$ 35.16

$C_3 = KCl(s)(300°-1043°) = (0.3115)(13.24)(743)(10^{-3}) =$ 3.06

$C_4 = KCl(l)(1043°-1680°) = (0.3115)(16)(637)(10^{-3}) =$ 3.17

$C_5 = KCl(g)(1680°-4600°) = (0.3115)(8.94)(2920)(10^{-3}) =$ 8.12

$$\sum_2^5 \Delta H + \sum_1^5 C = \qquad 149.45 \text{ kcal}$$

$$\Delta H_1 - \left[\sum_2^5 \Delta H + \sum_1^5 C \right] = 158.39 - 149.45 = \Delta H_6$$

$\Delta H_6 =$ heat absorbed in vaporizing fraction of $ZrO_2(l) =$ 8.94 kcal

$$\frac{8.94}{(0.6231)(100)} = 14.34\% \ ZrO_2(l) \rightarrow ZrO_2(g)$$

                                      158.39 kcal

Maximum adiabatic flame temperature limited by the boiling point of ZrO_2 is 4600°K.

Table III gives the calculated heats of reaction and maximum adiabatic flame temperatures for the compositions listed, and Table IV gives the theoretical reaction products existing at the maximum flame temperatures. Whereas most of the products of these metal-oxidant mixtures are shown to vaporize at the flame temperature, this is not the case with the zirconium mixtures. In Table IV, zirconium dioxide is shown to exist in the molten state at the calculated flame temperatures. The thermal stability and extremely high boiling point of ZrO_2 make possible the attainment of the highest calculated flame temperatures of the group by $Zr-KClO_4$ and $Zr-Ba(NO_3)_2$ mixtures.

All the mixtures of aluminum have heats of reaction high enough to bring the Al_2O_3 to its boiling point and to vaporize a portion of the oxide. The high heat of reaction of the $Al-KClO_4$ mixture leads to considerable dissociation of the products and the formation of a large quantity of condensible gases. In igniters, heavy confinement or extremely rapid reaction of this mixture leads to very high pressure peaks.

Heats of reaction of the magnesium mixtures are sufficient to raise the MgO to its boiling point and to vaporize a portion of it. The maximum flame temperatures of the magnesium mixtures, as with the aluminum and titanium mixtures, are determined by the boiling point of the metallic oxide product.

Because of the low boiling point of B_2O_3, the maximum flame temperatures of the boron mixtures are indicated to be somewhat below those of the other mixtures. The low boiling point of B_2O_3 also leads to the formation of large quantities of condensible gas at the flame temperature. It should be noted that the assumed mechanism for the reaction between boron and potassium nitrate is incorrect since heat-of-reaction measurements give higher than theoretical values at oxidizer loadings far below those used in these calculations. It has been postulated that the reaction of $B-KNO_3$ leads to the formation of KBO_2, potassium metaborate, as well as B_2O_3;[19] however, this was not considered in the calculations since thermochemical data on KBO_2 are not available.

As stated previously, the maximum flame temperatures that can be reached by the metal-oxidant compositions are in general limited to the temperature of vaporization of the metallic oxide. The quantity of condensible gases formed varies with each composition, but boron, magnesium, and aluminum fuels with $KClO_4$ or KNO_3 oxidizers have a greater tendency to vaporize the combustion products because of dissociation and high heats of reaction.

IGNITIBILITY TESTS

Initial consideration of an approach to study performance
characteristics of experimental igniter materials indicated that studies
of propellant ignitibility[20-23] were of sufficient interest to warrant a
refinement of technique in order to evaluate igniter materials further
for use in rocket igniters. To this end, equipment and techniques were
developed to yield data showing the relative quantity of igniter material
required to ignite a propellant sample and the action time of the igniter
from photocell measurements of the luminous intensity as a function of
time in a closed bomb.

Tests with black powder and JPN propellant indicated that
ignition was achieved in as short a time as 25 msec, but since marginal
quantities of igniter materials were being used, the ignition times
varied from 25 msec up to several seconds. For experimental con-
venience, ignition of the propellant sample was recorded as having
occurred when sufficient radiation was emitted for detection of its
combustion by an infrared sensitive photocell within 1 sec after
initiation of the igniter material. Fizz burning (nonluminous) of the
propellant and hangfires of greater duration than 1 sec were classed
as nonignitions.

APPARATUS AND PROCEDURE

The closed-bomb test chamber used in these experiments is
shown in Fig. 1. It is fitted with five quartz observation ports for light
transmission. The chamber has internal dimensions of 1 by 6 in. with
a free volume of 61 cc. A small sample of propellant ($\frac{1}{2}$-inch OD by
$\frac{1}{8}$-inch thick) is mounted in the receptacle approximately $3\frac{3}{5}$ in. above
the base of the crucible containing igniter powder. Ignition of the
powder is accomplished by passing current through a short length of
wire embedded in the powder. Figure 2A shows a block diagram of the
instrumentation used to follow the ignition process with photocells, and
Fig. 2B is a block diagram of the apparatus. In effect the photocell
nearest the igniter sample is used to observe the flash from the burning
igniter powder, and the other photocells observe the light emission from
the propellant when it begins to burn with a luminous flame. The output
from the photocells is fed to a Dumont Type 322 cathode-ray oscillo-
graph, a time base is provided by a Tektronix Type 180 Time Mark
Generator, and the transient phenomena shown on the screen of the
oscillograph are photographed with a Fairchild Oscillo-Record Camera.

For ignitibility tests, a small amount of powder is accurately weighed into the crucible and fired, the resultant ignition or nonignition of the propellant is determined either by observation or by examination of the film record. The statistical method used to determine the ignition probability is given by Churchman.[24] By this method, it is necessary to establish from past experience or intuitively an estimated range of charge weights required to obtain ignition every time or not at all. A predetermined number of tests, at least five, are made within this range with charge weights varying in equal increments until all the tests at a given charge weight level result in ignition and all tests at some lower charge weight result in nonignition of the propellant sample. Treatment of the data by the Churchman method results in a value for the charge weight required for 50 or 95% probability of ignition.

Heats of explosion were measured in a Parr Oxygen Bomb Calorimeter under 20 atm of helium. The results of some of the heat-of-explosion measurements are plotted in Fig. 3. The relative burning time of each igniter mixture was determined by burning 120-milligram samples in the window bomb with photoelectric instrumentation and measuring the duration of the flash as displayed on the screen of the oscillograph and photographed on 35-mm film.

A description of the materials used in the ignitibility tests is given in Table V. All the igniter mixtures were dry blended manually except those containing zirconium powder, which were mixed wet with benzene.

DISCUSSION OF RESULTS

Initially, propellant ignitibility tests in this program were performed with black powder and JPN propellant. It was found that the moisture content of black powder, within specification limits, and the use of air instead of nitrogen in the closed bomb played relatively minor roles in the overall ignition process. It was also found that the total energy and rate of burning of the igniter powder are significant factors in determining the effectiveness of the powder in igniting a double-base propellant under the conditions of this test. The effect of particle size on the ignitibility results was illustrated by comparing A-5 and A-3 black powder in the closed bomb. Considerably larger quantities of the slower burning A-3 black powder than of the A-5 were required for the same ignition probability. It was found that the effectiveness of black powder in igniting the test propellant could be increased by various additives, which either increased the heat of reaction of the mixture, reacted with the propellant decomposition

products, or ejected molten materials that gave up their latent heats as they struck the propellant surface. An increase in effectiveness of 15 to 20% over A-5 black powder was obtained with mixtures of black powder and additives such as lead picrate and potassium dinitroaceto-nitrile. Since black powder is a relatively poor matrix for additives, emphasis was ected to pyrotechnic materials that evolve greater amounts of energy per unit weight and volume than does black powder.

This work to date has principally involved studies of five metal fuels: magnesium, aluminum, titanium, boron, and zirconium. The principal inorganic oxidizers used were potassium perchlorate, potassium nitrate, barium nitrate, and to some extent sodium nitrate. Magnesium received greatest attention in experimental investigations because it is believed to be representative of pyrotechnic fuels, many of its performance characteristics being typical for the group. Other metals and alloys were used in the investigations, but interest centered around the five metals. Heats of explosion, relative burning rates, ease of ignition, and gas volumes produced were measured experi-mentally for many of the compositions.

Figure 4A shows a representative intensity-time curve obtained from an ignition test of JPN with black powder, and Fig. 4B shows representative intensity-time curves from several igniter mixtures.

Table VI shows the results of tests with mixtures of magnesium and KNO_3, $KClO_4$, $NaNO_3$, and $Ba(NO_3)_2$ oxidizers. Initial tests per-formed with several compositions containing magnesium showed that the effectiveness of the powdered mixtures, as determined by the ignitibility tests, was highly dependent on the rate at which they evolved thermal energy. Therefore, an attempt was made to compare the relative effectiveness of these materials when their burning intervals (relative burning times) were more nearly the same. Factorial experi-ments were performed to determine the effect of particle size of fuel and oxidant in at least two mixture ratios on the burning time of the igniter mixtures. It was found that, when $KClO_4$ was used as the oxidant in the dry powdered mixtures, the shortest burning intervals (fastest burning) were obtained when the fuel was very fine and the perchlorate was coarse in comparison.

In the ignitibility tests, the fast-burning $Mg-KClO_4$ mixtures contained magnesium that would pass a 200-mesh screen and be retained on a 325-mesh screen and coarse perchlorate that would pass a 100-mesh screen and be retained on a 140-mesh screen. For nitrate oxidizers, as would normally be expected, the fastest burning mixtures

were those containing finely divided fuel and oxidant. In the ignitibility tests, the magnesium used would pass a 200-mesh screen and be retained on a 325-mesh screen, and the oxidizers, KNO_3, $NaNO_3$, and $Ba(NO_3)_2$, were each sieved to pass a 200-mesh screen and be retained on a 325-mesh screen. Burning times measured for mixtures containing either perchlorate or nitrate oxidizers were thus placed on a comparable basis, as seen in Table VI. The reason for the difference in particle sizes required for rapid reaction of perchlorate versus nitrate oxidizers with magnesium fuel is apparently due in part to a bulk-density effect. It appears that the coating of magnesium powder on potassium perchlorate crystals results in faster burning than when Mg is coated with $KClO_4$ in dry powdered mixtures. Attempts were made to purify the oxidizers, but ignitibility tests and burning-time measurements indicated no significant performance difference between Reagent Grade and recrystallized oxidizers used in the igniter mixtures.

From the data shown in Table VI, it is difficult to draw strong conclusions concerning the effects of heat of explosion, total energy evolved from the igniters, relative burning times, relative rate of heat evolution, or gas volumes on the ignitibility effectiveness of these compositions. None of the compositions gave best performance for their individual group when the mixture ratios were designed to give the highest heats of explosion. Smaller quantities of igniter material were, however, required to ignite the double-base JPN test propellant as the Mg-KNO_3 and Mg-$NaNO_3$ compositions became more fuel rich, whereas the best performance from the Mg-$KClO_4$ and Mg-$Ba(NO_3)_2$ mixtures was obtained with the higher oxidizer containing compositions irrespective of heat of explosion. The best Mg-KNO_3 composition, igniter 57, has about 2.4 times the "igniting power" of A-5 black powder under the same conditions. Similarly, igniter 57 with a heat of explosion of about 1300 cal/g has almost twice the "igniting power" of igniter 51 (Mg and $KClO_4$), which has a heat of explosion of 2300 cal/g.

The effect of mixture ratio on the burning time is illustrated in Table VI. For mixtures of Mg and KNO_3, Mg and $Ba(NO_3)_2$, and Mg and $NaNO_3$ as the fuel content increases over the range tested, the relative burning time decreases indicating increasing reaction rate. For the Mg-$KClO_4$ compositions as the fuel content increases, the burning time increases indicating decreasing reaction rate.

The permanent gas volume produced is higher for the nitrate oxidizer mixtures, but since the reaction temperatures are higher for the Mg-$KClO_4$ mixtures, the maximum pressures developed in the closed bomb were higher for the Mg-$KClO_4$ mixtures. The data in

Tables VI and VII showing the measured gas volume produced by several of the mixtures indicates the significant influence of pressure in determining propellant ignitibility under the conditions of this test.

The indication that igniter mixtures containing KNO_3 as oxidizer are more efficient than the hotter mixtures containing $KClO_4$ oxidizer seemed unusual (in spite of the fact that $KClO_4$ contains 46.2% available oxygen and KNO_3 contains only 39.6% based on formation of KCl and K_2O combustion products). Additional investigations were made. It was found that, when Mg-KNO_3 mixtures were burned in the closed bomb in the absence of a propellant sample under helium or nitrogen, the residue from this combustion exploded when contacted by moist air or water. It was also observed that

1. Stoichiometric mixtures of Mg (38%) and KNO_3 (62%) based on formation of MgO and K_2O showed normal behavior in ignitibility tests and did not give products capable of secondary burning when exposed to moist air.

2. As the magnesium content of the binary mixtures was increased successively from 38 to 60%, the quantity of material capable of secondary burning increased.

3. When fuel-rich Mg-KNO_3 mixtures were burned in the presence of the test propellant in the closed-bomb ignitibility apparatus, the secondary burning effect was observable only in those cases where the propellant sample had not shown any tendency to ignite.

4. Since the products capable of secondary burning had spent themselves in every case where propellant ignition occurred, it appeared obvious that reaction occurred between the propellant combustion products and those of the igniter. It is believed that reaction of the igniter combustion products with the initial decomposition products of the propellant at or near the surface of the propellant either liberated sufficient energy to aid in ignition of the propellant or triggered further reaction of the propellant gases themselves.

5. If the secondary combustion reaction were due to "hot particles" or magnesium metal reacting with propellant gases, such effect would have been more pronounced with the hotter Mg-$KClO_4$ mixtures. This was not found.

6. If the secondary reaction were due to formation of Mg_3N_2 and subsequent reaction with propellant, this would have been noted in

the fuel-rich $Mg-KClO_4$ mixtures since the inert gas generally used in the closed bomb is nitrogen.

7. Several tests with Mg and $NaNO_3$ (fuel rich) indicated that a similar effect was produced by this reaction, but the effect was not so pronounced as with KNO_3.

It is postulated that the increased effectiveness of fuel-rich $Mg-KNO_3$ mixtures as igniters is due to the liberation of free potassium from the igniter combustion products. Because of extreme affinity for oxygen and high thermal stability of the oxide, magnesium in excess at high temperatures combines with the oxygen from dissociating K_2O liberating elemental potassium. Brewer[11, 12] has shown that K_2O as a gaseous species is virtually nonexistent and only Li_2O of the alkali metal oxides may exist as a stable gas. Since the stability of the alkali oxides increases in the order Li > Na > K > Rb > Cs, only potassium, rubidium, and cesium oxides would be readily reduced to their elemental form, whereas sodium oxide would be less likely to show this effect and lithium oxide would probably not show this effect at all.

Because such a large increase in ignition performance is shown by this reaction, it is clear that additional work should be done to determine if advantage can be taken of this type of reaction using metals that are more stable to corrosion than magnesium.

Table VII shows the results obtained from ignitibility tests with various igniter mixtures; it is seen that the boron mixtures gave best performance based on the quantity of material required to ignite the test propellant. The $B-KClO_4$ mixtures were almost as effective in igniting the propellant sample as the best magnesium compositions. Burning-time measurements of compositions shown in Table VII, as well as many others not shown, indicate that for mixtures of B and KNO_3, B and $KClO_4$, Ti and $KClO_4$, Zr-Ni and $KClO_4$, and Ti and $Ba(NO_3)_2$ the reaction rate increases as the fuel content is increased past stoichiometric. Burning times measured for compositions containing Al and $KClO_4$ or Al and $Ba(NO_3)_2$ were found to be insensitive to small changes in composition.

Composition 118 in the $B-KNO_3$ series showed best performance with the highest measured heat of explosion and reaction rate for the group, whereas oxygen-rich composition 121 with the lowest heat of explosion and lowest reaction rate was next best. Of the $B-KClO_4$ igniters, oxygen-rich composition 125 with the lowest heat of explosion and lowest reaction rate was the most efficient in its group. Other

mixtures in the B-KClO$_4$ series showed poorer performance as the
reaction rate and heat of explosion increased.

The titani um mixtures were found to be the least efficient of
those tested. Compositions 104 and 105 with KClO$_4$ oxidizer showed
effectiveness only slightly better than black powder, whereas the
Ti-Ba(NO$_3$)$_2$ mixture, composition 106, was found to be less effective
than A-5 black powder under the test conditions. It is believed that this
is due partly to the mode of burning of these mixtures. All the mixtures
tested except the binary titanium-oxidant mixtures formed finely divided
amorphous powders as combustion products, which were thoroughly
coated on all interior parts of the bomb assembly. The titanium-oxidant
mixtures, however, formed a molten mass of residue in the form of
slag, which remained in or near the igniter container. The distribution
of combustion products from the titanium mixtures in the ignitibility
chamber was poor compared with that obtained from the magnesium or
boron mixtures.

Compositions containing flake aluminum were difficult to ignite
from a hot wire, but ignitibility test data obtained with igniters 85 and
86 showed performance comparable to that obtained with magnesium
fuel. Atomized aluminum would not ignite at all from a glowing wire,
but it was found that the addition of titanium metal powder to these
mixtures resulted in easier ignition and measured heats of explosion
approached the theoretical maximum. The formation of a molten glob
of residue, as was found with titanium mixtures, was virtually elimi-
nated in mixtures containing aluminum and titanium. Igniter T-1
containing atomized aluminum and titanium fuels, shown in Table VII,
gave effective ignition of the propellant and showed a reaction time
shorter than that measured for titanium or aluminum compositions
individually. Considerable work has been done to exploit the advantages
of this fuel combination, and performance was proved in many rocket-
motor firings under the most adverse conditions.

Zirconium-nickel alloy (70/30) was found to be the slowest
burning fuel tested. Igniter 95 showed only slightly greater ignition
effectiveness than that obtained with the titanium mixtures or A-5
black powder.

Igniters containing zirconium metal powder in granular form
could not be ignited from a hot wire, and consequently, no measure-
ments were made with these mixtures. Pyrophoric zirconium powder
has, however, been used extensively in investigations of fuels for squibs
this laboratory. This powder is manufactured by reduction of

powdered ZrO_2 with excess calcium and is sensitive to ignition. Measurements of reaction time with stoichiometric $Zr-Ba(NO_3)_2$ mixtures (Zr approximately 6 μ with Fisher Sub-Sieve Sizer) indicate relative flash duration times less than one-half those of the fastest burning mixtures of boron or magnesium. Squibs containing zirconium fuel have been found to be extremely effective in initiating the most difficultly ignitible pyrotechnics under conditions of low confinement.

BORON-FUEL INVESTIGATION

The commercial preparation of amorphous boron is rather a crude process, and critical performance reproducibility of certain types of igniters containing boron may be difficult to obtain if careful controls are not exercised. In cooperation with the Redstone Division of the Thiokol Chemical Corporation, several parameters relating to the properties of boron for igniters were investigated. It was found at Thiokol that "rolled-tube"-type igniters prepared with certain lots of boron gave excellent performance in overall ignition times of rocket motors fired at low temperatures, whereas other lots gave marginal or extremely poor performance. Chemical analyses by "wet methods" failed to resolve the lot-to-lot performance variations observed. From Table VIII, it is seen that the total boron content of the various lots tested ranged from 65 to over 90%, and particle-size measurements by sub-sieve methods show minor differences.[25]

Attempts were made to characterize elemental boron using spectrographic analysis, X-ray diffraction, and electron microscopy techniques. In addition, it seemed appropriate to subject powdered samples of boron mixed with an oxidant to the closed-bomb combustion test in which the flash intensity is measured as a function of time. Approximately 22 samples of boron from separate lots were tested. The suppliers or manufacturers of the boron tested were Fisher Scientific Company, F. W. Berk & Co., Inc., American Potash & Chemical Corp., Cooper Metallurgical Associates, Arthur S. La Pine & Co., and Metalsalts Corporation.

No correlation with performance of the various samples could be made on the basis of electron microscopy or spectrographic analysis. Examination indicated that the impurities present corresponded to the composition of firebrick. Some correlation was possible, however, from X-ray diffraction patterns. Good correlation was obtained in comparing the results of closed-bomb combustion tests with actual performance of igniters fired in rocket motors at low temperatures.

Twenty-two samples of boron were intimately mixed with potassium perchlorate in the ratio

Boron   20.6%
$KClO_4$ 79.4% (100% through 325 mesh)

Aliquot portions of each of the 22 mixtures (120 mg) were burned in the window bomb with photoelectric instrumentation to determine the relative flash intensities, the rate of rise of light intensity, and the flash duration. Marked differences in the intensity-time curves were obtained; in particular, it was found that many of the boron samples burned very rapidly, whereas others showed sluggish reaction. The representative intensity-time curves shown in Fig. 5 indicate the three distinct classifications that were obtained based on flash duration (relative reaction time). Of the 22 samples tested, six were found to react rapidly and give a time-intensity curve similar to that shown by curve A in Fig. 5, six samples gave curves similar to that represented by curve B, and 10 samples were found to be very slow burning giving curves similar to the one represented as C. Curve A has a characteristically high relative intensity, rapid rise rate, and short duration. Curve B has a high relative intensity, medium to rapid rise rate, and a duration of two to three times that of curve A. Curve C has a low relative intensity, low rise rate, and very long duration.

Actual rocket-motor firings at −50°F made by Thiokol indicated that igniters prepared from boron which exhibited rapid reaction in closed-bomb tests, Fig. 5, curve A, gave short, reproducible overall ignition delays, whereas the slow-burning samples of boron, Fig. 5, curve C, gave long ignition delays. It should be noted that the criteria for determining the suitability of the various lots of boron were based on tests in one type of motor with a particular igniter design. There are undoubtedly many igniter applications where the reaction rate of the boron used would either not be detected or would not significantly affect the ignition results.

Table VIII gives the average flash duration measured from five tests of each of the 22 mixtures, arranged in order of decreasing reaction rate. The best samples tested from the standpoint of reproducibility and combustion kinetics were those containing magnesium and sodium in a combined form (solid solution) with the boron called "Reactive Boron," manufactured by American Potash & Chemical Corp. The slowest burning samples were those containing very pure boron produced by electrolytic reduction. Crystalline boron produced by electrolysis, when mixed with $KClO_4$ and burned in the window bomb,

showed a burning time of 233 msec as opposed to 17.7 msec for a sample cor. ining "Reactive Boron." (Crystalline boron was reported to contain 9..2% B but only 92% was actually found.) This was somewhat surprising, but Professor Speiser[26] has recently stated that pure boron, probably crystalline, is an inert substance that is very difficult to ignite even under oxygen pressure and, after ignition by the addition of other fuels, shows very sluggish combustion.

Synthetic mixtures prepared by adding B_7O to fast-burning boron samples and finely divided magnesium to slow-burning samples gave results showing decreased reaction rates with addition of B_7O and increased reaction rates with addition of magnesium. This effect was also found by the Bureau of Mines[27, 28] in their solid ramjet research.

X-ray diffraction studies of elemental boron[29] showed that the slow-burning grades of boron were those that showed peaks for "d" values of 5.06A, a characteristic line of crystalline boron, and 4.71A. Many of the slow-burning boron samples, which are brown in color, were found to contain a high proportion of boron suboxides. X-ray diffraction patterns made with a control sample of B_7O indicated that the chief suboxide present .n many of the borons was B_7O. It was also found that the slow-burning amorphous boron samples contained 10% or more B_7O, whereas the fast-burning samples showed negligible amounts of B_7O. The "d" values for B_7O are given in Table IX.

The outstanding factors found to affect combustion kinetics of boron adversely were (1) a high content of crystalline materials, particularly crystalline boron, and (2) a high content of lower oxides of boron, particularly B_7O.

CONCLUSIONS

1. Adiabatic flame temperature calculations show that zirconium-oxidant and aluminum-oxidant mixtures exhibit the highest flame temperatures of the mixtures studied. The maximum flame temperatures that can be reached by metal-oxidant compositions are, in general, limited to the vaporization temperature of the metallic oxide formed. When metal-oxidant compositions are burned at pressures above atmospheric, the increased boiling points of the products lead to corresponding increases in the flame temperatures and formation of larger quantities of condensible gases.

2. Data from closed-bomb ignitibility tests indicate that heats of explosion, flame temperatures, heats of condensation, reaction

products, and reaction rates are significant in determining the ignition effectiveness of various materials, but correlations based on simple analyses cannot be made. Metal-oxidant mixtures containing the fuels magnesium, boron, and aluminum gave good performance in small-scale ignitibility tests and have, in general, been found to give correspondingly desirable performance in rocket igniters. The ignitibility of aluminum compositions is greatly improved by addition of metals that react from their solid state, such as titanium or boron.

3. The content of crystalline materials and suboxides largely determine the reactivity of amorphous boron. Crystalline boron and amorphous boron containing a large proportion of suboxides show sluggish combustion, whereas boron with a very low suboxide content and dissolved "sensitizers" such as sodium or magnesium burns very rapidly.

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REFERENCES

1. Grosse, A. V., and Conway, J. B., "The Combustion of Metals," Research Institute of Temple University, First Technical Report, High Temperature Project, October 1951.

2. Levy, M. E., "A Determination of the Product Residues and Maximum Flame Temperatures of Several Primer Mixtures," Frankford Arsenal Report R-1206, May 1954.

3. Handbook of Chemistry and Physics, 36th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1954.

4. Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy. X. High-temperature Heat-content, Heat-capacity, and Entropy Data for Inorganic Compounds," Bureau of Mines, Bulletin 476, 1949.

5. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, February 1952.

6. Perry, J. H., _Chemical Engineers' Handbook_, 2d Edition, McGraw-Hill Book Company, Inc., New York, N. Y., 1941.

7. Smithells, C. J., _Metals Reference Book_, Interscience Publishing Company, Inc., New York, N. Y., 1949.

8. B ewer, L., "The Thermodynamic Properties of the Oxides and their Vaporization Processes," Chemical Reviews, 52, number 1, February 1953.

9. Bichowsky, F. R., and Rossini, F. D., _The Thermochemistry of Chemical Substances_, Reinhold Publishing Corp., New York, N. Y., 1936.

10. International Critical Tables, Vol. 7, p. 247.

11. Brewer, L., and Mastick, D. F., "Theoretical Calculations of the Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides," Journal of American Chemical Society, 73, May 1951.

12. Brewer, L., and Margrave, J., "The Vapor Pressures of Lithium nd Sodium Oxides," Journal of Physical Chemistry, 59, number 5, May 1955.

13. Altman, D., "The High Temperature Thermodynamics of Some Potassium and Sulphur Compounds," Jet Propulsion Laboratory Progress Report 1-47, April 1946.

14. Groves, W. O., Hoch, M., and Johnston, H. L., "Vapor Solid Equilibria in the Titanium-Oxygen System," Journal of Physical Chemistry, 59, number 2, February 1955.

15. Soulen, J. R., Sthapitanonda, P., and Margrave, J. L., "Vaporization of Inorganic Substances: B_2O_3, TeO_2 and Mg_3N_2," Journal of Physical Chemistry, 59, number 2, February 1955.

16. Speiser, R., Naiditch, S., and Johnston, H. L., "The Vapor Pressure of Inorganic Substances. II. B_2O_3," Journal of the American Chemical Society, 72, June 1950.

17. Brewer, L., and Search, A. W., "The Gaseous Species of the $Al-Al_2O_3$ System," Journal of American Chemical Society, 73, November 1951.

18. Emley, E. F., "Note on the Free Energies of Formation of the Fluorides, Chlorides and Oxides of the Alkali and Alkaline Earth

and Rare Earth Metals, and on the Occurrence in Fused Salt
Mixtures of Double Decomposition Reactions Involving these
Substances," Chemical Engineering Science, 1, number 3,
April 1952.

19. Thiokol Chemical Corporation, Redstone Division, Quarterly
    Progress Report 1-56, October-December 1955.

20. Goldhagen, S., and Zihlman, F. A., "Development of a Method
    for Determination of the Ignitability of Propellants," U. S. Naval
    Powder Factory NAVORD Report 3011, May 1952.

21. "Development of a Method for the Determination of Both the
    Ignitability of Double-Base Rocket Propellants and the Effective-
    ness of Various Types of Igniter Compositions in Igniting Double-
    Base Rocket Propellants," Picatinny Arsenal Monthly Progress
    Report 5, January 1953.

22. Gowen, L. F., and Elzufon, E. E., "Closed Bomb and Gun Studies
    of Various Metal Oxidant Mixtures as Igniters for Propellants,"
    Bulletin of the First Symposium on Solid Propellant Ignition,
    September 1953.

23. Goldhagen, S., and Zihlman, F. A., "An Evaluation of the Naval
    Powder Factory Ignitability Method using Ignition Systems other
    than Black Powder," Bulletin of the First Symposium on Solid
    Propellant Ignition, September 1953.

24. Churchman, C. W., "Statistical Manual Methods of Making
    Experimental Inferences," 2d Edition, Pitman-Dunn Laboratory,
    Frankford Arsenal, Philadelphia, Pa., June 1951.

25. Pelham, J., and Anderson, F., Thiokol Chemical Corporation,
    Redstone Division, personal communication.

26. Speiser, R., (Professor), Ohio State University, personal
    communication.

27. Herickes, J. A., Richardson, P. A., and Ribovich, J., "Com-
    bustion of Solid Fuels for Ram Jets," Bureau of Mines, Pittsburgh,
    Pa., Progress Report 28, January-March 1953.

28. Herickes, J. A., Richardson, P. A., and Ribovitch, J., "Com-
    bustion of Solid Fuels for Ram Jets," Bureau of Mines, Pittsburgh,
    Pa., Progress Report 29, April-June 1953.

29. Redstone Arsenal Report 3M7N12, Monthly Report for Rocket
    Development Laboratory, Rocket Development Division, 29 July
    1955, Confidential.

Table 1
Thermochemical Constants

Species	Mol. Wt.	Heat of Formation, kcal/mole at 298°K	Melting Point, °K	Heat of Fusion, kcal/mole	Boiling Point, °K	Heat of Vaporization, kcal/mole	Vaporization Products	References
Zn	91.22	0	2125		>3200			3, 5, 6
ZrO_2	123.22	258.4	3000	20.8	4573	92 to 117	$ZrO_2(g)$	3, 5, 8, 10
Al	26.97	0	933	2.6	2600	67.9		3, 5, 6
Al_2O_3	101.94	399	2318	26.0	3800	456 diss.	$AlO(g) + O(g)$	3, 5-9, 17
Mg	24.32	0	923	2.2	1393	31.5		3, 5, 6
MgO	40.32	145.7	2900	18.5	3350	80 to 100	$MgO(g)$	3, 5-8
Ti	47.90	0	2100		>3300	112.7		3, 5, 6
TiO_2	79.90	214.1	2100	11.4	3000	63 to 77	$TiO(g) + O(g)$	3, 6, 10
Ti_2O_3	143.80	367	2400	≅16	3300	280 diss.	$TiO(g) + O(g)$	3, 5, 8, 14
B	10.82	0	2600		2800			3
B_2O_3	69.64	302	723	5.5	2520	77.6	$B_2O_3(g)$ >2500°K diss.	3, 4, 5, 8, 15, 16
$KClO_4$	138.55	112.71						3, 9
KCl	74.55	104.3	1043	6.1	1680	38.8	$KCl(g)$ >2500°K diss.	3, 5, 7, 13, 18
KNO_3	101.1	118.78						3
K_2O	94.2	86.3			1750 sub.	189 diss.	$K(g) + O(g)$	3, 8, 11, 12, 13, 18
$Ba(NO_3)_2$	261.38	238.28						3
BaO	153.4	133.1	2190	12.5	2273	76.5	$BaO(g)$ >3000°K diss.	3, 5-8, 11, 18

Table II
Heat-capacity Data

| Species | $C_p = a + b \times 10^{-3}T + c \times 10^5 T^{-2}$ | | | Temperature Range, °K | Avg C_p | Reference |
	a	b	c			
$ZrO_2(s)$	11.62	10.64	−1.78	300 to 1673		7
$ZrO_2(l)$				3000	35	*
$Al_2O_3(s)$	27.43	3.06	−8.47	300 to 1800		4
$Al_2O_3(l)$				2300 to 3800	35	17
$MgO(s)$	10.18	1.74	−1.48	300 to 2100		4
$MgO(g)$	8.64	0.20	−0.75	300 to 3000		'
$TiO_2(s)$	17.97	0.28	−4.35	300 to 1800		4
$Ti_2O_3(a)$	7.31	53.52		300 to 473		4
$Ti_2O_3(\beta)$	34.68	1.30	−10.20	473 to 1800		4
$Ti_2O_3(l)$				2400 to 3300	40	*
$B_2O_3(s)$	8.73	25.4	−1.31	300 to 723		4
$B_2O_3(l)$				723 to 1800	30.5	4
$B_2O_3(g)$					25	*
$KCl(s)$	9.89	5.2	0.77	300 to 1043		4
$KCl(l)$				1043 to 1200	16.0	4
$KCl(g)$	8.94		−0.24	300 to 2000		4
$K_2O(s)$				300 to 1200	18.8	*
$BaO(s)$	9.79	5.21		300 to 1000		4
$BaO(l)$					18	*
$BaO(g)$					10	*

*Estimated by Kopp's rule or by the "rough-and-ready" generalities discussed by Kelley.[4]

Table III
Calculated Heats of Reaction and Maximum Adiabatic
Flame Temperatures of Stoichiometric Metal-Oxidant Igniter Mixtures

Composition	Ratio	Heat of Reaction (Calc.), cal/g	Maximum Adiabatic Flame Temp, °K
$Zr-KClO_4$	56.8/43.2	1584	4600
$Zr-Ba(NO_3)_2$	46.6/53.4	1105	4000
$Zr-KNO_3$	53.0/47.0	1149	3500
$Al-KClO_4$	34.2/65.8	2490	3800
$Al-Ba(NO_3)_2$	25.6/74.4	1594	3800
$Al-KNO_3$	30.8/69.2	1761	3800
$Mg-KClO_4$	41.2/58.8	2433	3350
$Mg-Ba(NO_3)_2$	31.8/68.2	1627	3350
$Mg-KNO_3$	37.5/62.4	1784	3350
$Ti-KClO_4$	48.0/52.0	1805	3300
$Ti-Ba(NO_3)_2$	37.9/62.1	1204	3300
$Ti-KNO_3$	44.2/55.8	1275	3300
$B-KClO_4$	17.2/82.8	2356	3340
$B-Ba(NO_3)_2$	12.1/87.9	1341	2520
$B-KNO_3$	15.2/84.8	1495	2520

Table IV

Theoretical Reaction Products in Moles at Maximum Flame Temperature Produced
by 100-gram Stoichiometric Mixtures of Metal-Oxidant Igniters

Products at Flame Temperature	Zr-KClO4	Zr-KNO3	Zr-Ba(NO3)2	Al-KClO4	Al-KNO3	Al-Ba(NO3)2	Mg-KClO4	Mg-KNO3	Mg-Ba(NO3)2	Ti-KClO4	Ti-KNO3	Ti-Ba(NO3)2	B-KClO4	B-KNO3	B-Ba(NO3)2
$Zr-O_2(l)$	0.534	0.501	0.511												
$Zr-O_2(g)$	0.009														
$KCl(g)$	0.081			0.328						0.334			0.514		
$K(g)$	0.230	0.465		0.147	0.664		0.054	0.618		0.041	0.552		0.083	0.838	
$Cl(g)$	0.230			0.147			0.054			0.041			0.083		
$O_2(g)$		0.079		0.205	0.036	0.078	0.370	0.128					0.092	0.209	
$O(g)$		0.074	0.043	0.410	0.075	0.194		0.054					0.046		
$N_2(g)$		0.232	0.204		0.342	0.285		0.309	0.261		0.276	0.237		0.419	0.336
$BaO(g)$			0.161			0.247			0.261			0.237			0.336
$Ba(g)$			0.043			0.036									
$Al_2O_3(l)$				0.359	0.521	0.371									
$AlO(g)$				0.546	0.100	0.208									
$MgO(l)$							0.378	1.174	0.752						
$MgO(g)$							1.316	0.370	0.553						
$Ti_3O_5(l)$										0.125	0.387	0.271			
$TiO_2(g)$										0.375	0.074	0.125			
$TiO(g)$										0.375	0.074	0.125			
$B_2O_3(l)$													0.566	0.275	
$B_2O_3(g)$													0.462	0.430	0.561
$HO(g)$															
Total moles	1.164	1.431	0.962	2.142	1.760	1.421	2.172	2.653	1.827	1.291	1.363	0.995	1.846	2.171	1.233
Total gas	0.630	0.632	0.451	1.763	1.239	1.050	1.794	1.479	1.075	1.166	0.939	0.724	1.846	1.896	1.233
Permanent gas	0.000	0.232	0.204	0.000	0.342	0.264	0.000	0.309	0.261	0.000	0.276	0.237	0.000	0.419	0.336

Table V
Materials Used in Ignitibility Tests

Aluminum (atomized)	Reynolds type 120, 85% through 325 mesh, 99+% pure
Aluminum (flake)	Merck, 60% through 200 mesh, 40% through 325 mesh
Magnesium	(ground, dichromated) 100% through 200 mesh and retained on 325 mesh, 97.5% free magnesium
Titanium (degassed)	Metal hydrides, 100% through 325 mesh, 96.7% titanium
Boron (amorphous)	Fisher, total boron content 80%, less than 1μ average particle diameter (Fisher Sub-sieve Method)
Zirconium (granular)	Foote Mineral Company, 100 mesh $\times$ 10μ
Zirconium (powder)	Metal Hydrides, 100% through 200 mesh
Zirconium-Nickel Alloy powder	70/30 Metal Hydrides, 100% through 325 mesh
Potassium Perchlorate (Reagent Grade)	
Potassium Nitrate (Reagent Grade)	
Barium Nitrate (Reagent Grade)	
Sodium Nitrate (Reagent Grade)	

Nominal Composition of JPN Propellant, Wt. %

Nitrocellulose (13.25% N)	51.40
Nitroglycerin	42.90
Diethyl phthalate	3.23
Ethyl centralite	1.00
Potassium sulfate	1.25
Carbon black	0.20
Candelilla wax	0.02

Table VI

Measurements with Magnesium-Oxidant Mixtures Using JPN Propellant in Ignitibility Tests

Igniter Number	Nominal Composition, wt %		Measured Heat of Explosion, H, cal/g	Wt. Required for 50% Probability Ignition, w, mg	Total Heat Evolved, wH, cal	Relative Burning Time, t, msec	Relative Rate of Heat Evolution, r = wH/t, cal/msec	Measured Gas Volume at S.T.P., cc/g
	Mg	Oxidizer						
58	65	35 KNO_3	1327	72.5	96.2	18.0	5.34	58.0
57	60	40 KNO_3	1315	66.5	87.5	19.6	4.46	58.0
55	55	45 KNO_3	1515	76.5	116.0	22.6	5.13	64.0
53	50	50 KNO_3	1658	88.5	146.7	26.4	5.55	65.3
56	45	55 KNO_3	1680	98.5	165.5	28.3	5.85	67.6
54	38	62 KNO_3	1674	108.5	181.6	40.5	4.47	63.0
52	50	50 $KClO_4$	2158	131.5	283.8	24.1	11.78	13.1
51	45	55 $KClO_4$	2300	115.5	265.6	22.4	11.85	15.6
49	40	60 $KClO_4$	2203	105.5	232.4	19.6	11.80	22.7
50	37	63 $KClO_4$	2050	98.5	202.0	17.8	11.35	44.9
84	60	40 $NaNO_3$	1742	73.5	128.0	17.0	7.52	
83	50	50 $NaNO_3$	1933	83.5	161.4	21.7	7.44	83
30	50	50 $Ba(NO_3)_2$	1516	100.5	152.3	14.5	10.50	15
61	45	55 $Ba(NO_3)_2$	1553	94.5	146.7	15.8	9.28	
60	40	60 $Ba(NO_3)_2$	1583	90.5	143.3	17.5	8.19	
37	32	68 $Ba(NO_3)_2$	1484	88.5	131.3	22.0	5.96	60
A-5	Black powder		711	160.2	113.9	34.0	3.35	
A-3	Black powder		≈711	207.6	147.6	52.0	2.83	224.0

Table VII

Propellant Ignitibility Tests with Various Igniter Mixtures

Igniter Number	Nominal Composition, wt %° Fuel Oxidizer°	Measured Heat of Explosion, H, cal/g	Wt. Required for 50% Probability Ignition, w, mg	Total Heat Evolved, wH, cal	Relative Burning Time, t, msec	Relative Rate of Heat Evolution, r = wH/t, cal/msec	Measured Gas Volume at S.T.P., cc/g
118	30 B 70 KNO$_3$	1603	85.5	137.0	26.5	5.17	103
119	25 B 75 KNO$_3$	1410	96.5	136.1	33.0	4.12	
120	20 B 80 KNO$_3$	1280	90.5	115.8	39.4	2.94	89.0
121	15 B 85 KNO$_3$	1100	88.5	97.3	51.0	1.91	90.6
122	30 B 70 KClO$_4$	1323	114.5	151.5	28.2	5.37	40.8
123	25 B 75 KClO$_4$	1219	79.5	96.9	24.1	4.02	
124	20 B 80 KClO$_4$	1148	75.5	86.7	32.1	2.70	
125	15 B 85 KClO$_4$	1003	72.5	72.7	38.5	1.88	115
126	25 B 75 Ba(NO$_3$)$_2$	330	106.5	141.6	41.7	3.39	
104	50 Ti 50 KClO$_4$	1740	154.5	268.8	57.4	4.68	67
105	55 Ti 45 KClO$_4$	1620	151.5	245.4	53.0	4.63	63
106	30 Ti 70 Ba(NO$_3$)$_2$		197.5		86.0		
86	30 Al† 70 KClO$_4$	2250	98.5	221.6	78.2	2.83	
85	35 Al† 65 KClO$_4$	2365	95.5	225.8	86.8	2.60	
T-1	22.2 Al† 63.5 KClO$_4$ 14.3 Ti	2167	92.5	200.4	29.8	6.72	<50
95	50 Zr-Ni 50 KClO$_4$	1209	141.5	171.1	120.0	1.42	

°Oxidizers 100% through 200-mesh and retained on 325-mesh screen.
†Flake.
‡Atomized.

Table VIII
Measurements Made on Various Boron Samples

Sample Designation	Source	Particle* Size, μ	Total† Boron Content, %	Type Curve, Fig. 4	Flash Duration, ‡ msec
WS#4§	American Potash & Chemical Corp.	0.50	69.7	A	17.7
Fisher	Fisher Scientific Company	0.62	80.4	A	27.3
B-3	F. W. Berk & Co., Inc.	0.65	81.3	A	27.7
P-124, 125§	American Potash & Chemical Corp.	0.81	70.3	A	30.3
WS#2§	American Potash & Chemical Corp.	0.54	70.5	A	34
B-4	F. W. Berk & Co., Inc.	0.70	73.2	A	38
Trona	American Potash & Chemical Corp.	0.86	90.7	B	69
B-19	F. W. Berk & Co., Inc.	0.96	80.7	B	77
B-6	F. W. Berk & Co., Inc.	0.95	79.6	B	83
B-14	American Potash & Chemical Corp.	0.88	91.8	B	83
B-12	American Potash & Chemical Corp.	0.90	90.3	B	87
B-17	American Potash & Chemical Corp.	0.90	89.3	B	87
B-10	F. W. Berk & Co., Inc.	0.90	86.6	C	112
La Pine	Arthur S. La Pine & Co.		65.3	C	121
B-7	F. W. Berk & Co., Inc.	0.98	86.1	C	125
B-9	F. W. Berk & Co., Inc.	1.01	86.5	C	126
B-8	F. W. Berk & Co., Inc.	1.06	86.9	C	128
B-11	F. W. Berk & Co., Inc.	1.00	85.3	C	152
Metalsalts	Metalsalts Corporation	1.01	85.2	C	155
B-5	F. W. Berk & Co., Inc.	1.17	90.0	C	194
B-13	American Potash & Chemical Corp.	1.2	88.3	C	195
Cooper	Cooper Metallurgical Associates	1.9	92.0	C	233

*Fisher Sub-Sieve Analysis by Thiokol Chemical Corporation, Redstone Division.[26]

†By Na_2CO_3 fusion and titration with NaOH in presence of mannitol, measured by Thiokol Chemical Corporation, Redstone Division.[25]

‡ From initial detection of radiant intensity to a point which represents 10% of maximum intensity on the decay portion of intensity-time curve, when burned with $KClO_4$.

§"NAR" Grades of boron containing sodium and magnesium.

Table IX
Characteristic Lines of B_7O from X-ray Diffraction

Interplanar Spacing "d" Value, angstroms	Relative Intensity $I*/I$
4.17	52
3.77	16
2.60	100
2.30	62
2.19	9
1.87	7,
1.70	7
1.65	7
1.47	15
1.44	17

*Intensity of line relative to strongest line = 100.

PRESSURE PICKUP (OPTIONAL)

TOP CLOSURE

RECEPTACLE SCREW

PROPELLANT RECEPTACLE

WINDOW RETAINER

QUARTZ WINDOW

HOT WIRE

IGNITER CRUCIBLE

BOMB BODY

ELECTRODES

BOTTOM CLOSURE

INTERIOR ASSEMBLY
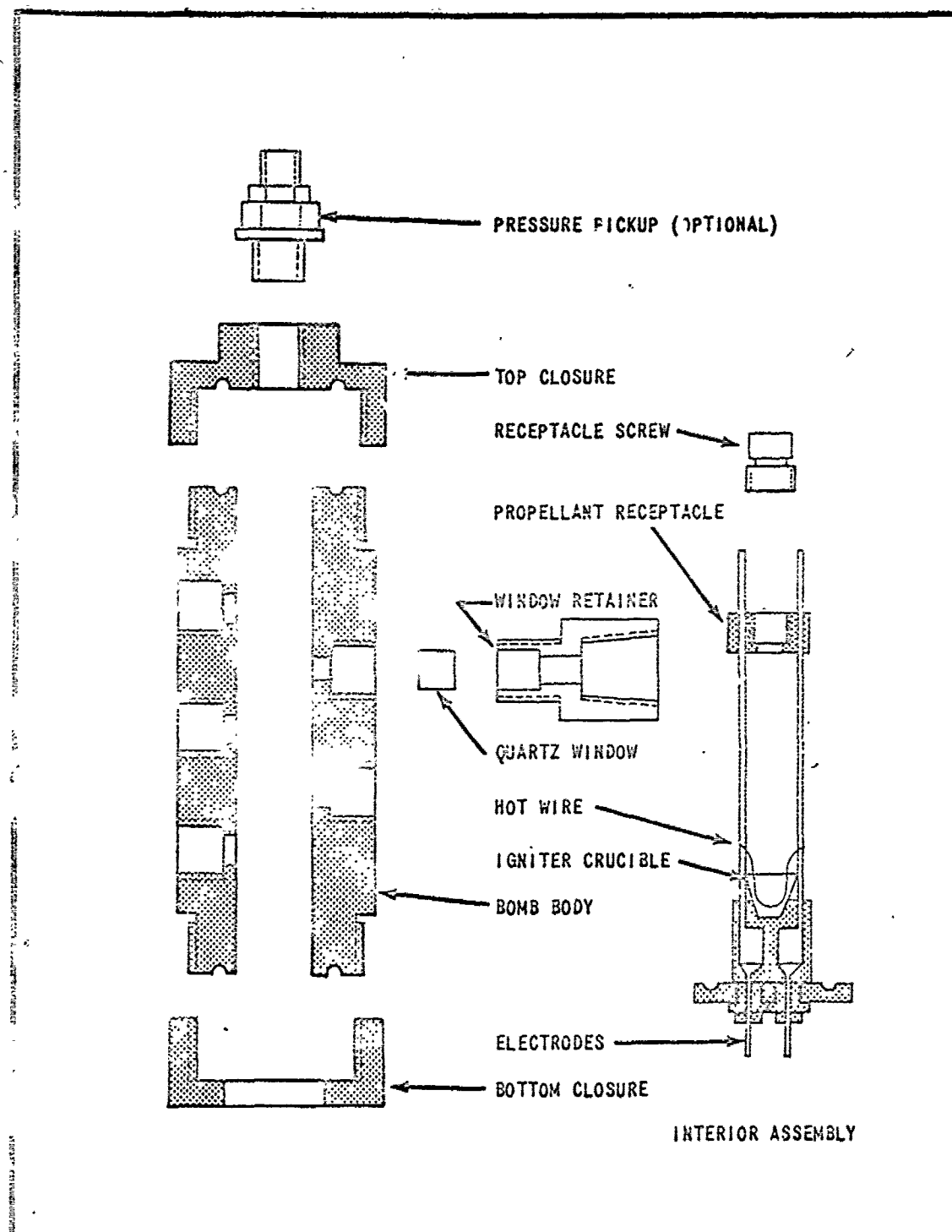
FIG. 1   WINDOW BOMB FOR IGNITION STUDIES

CONFIDENTIAL
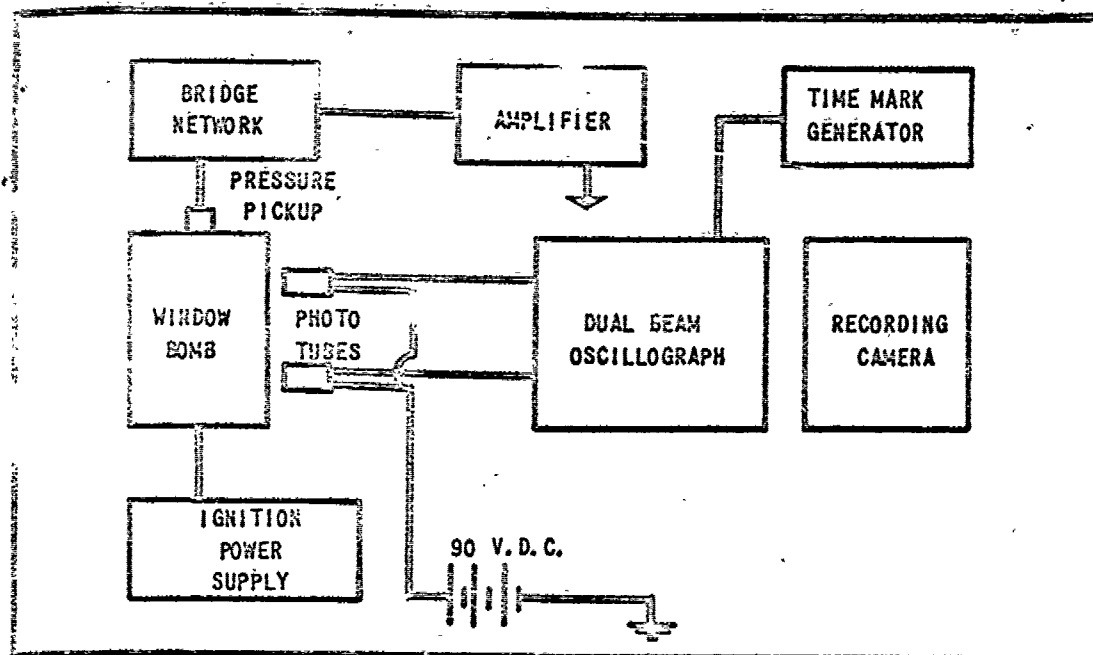
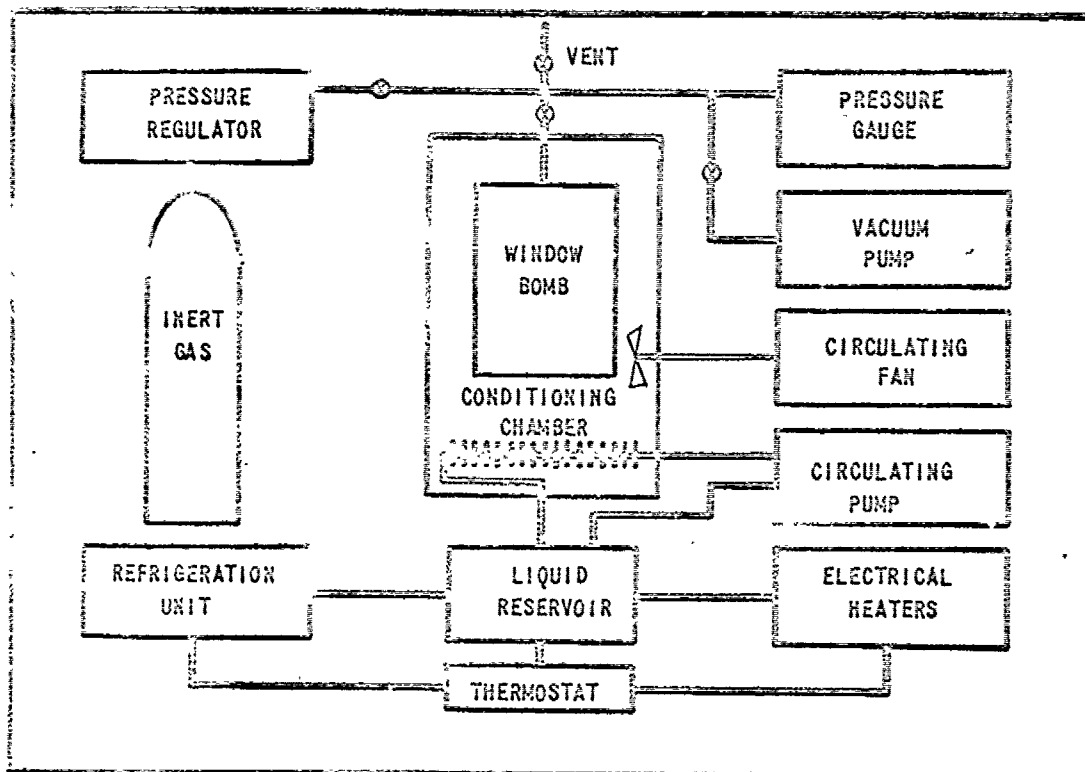FIG. 2a BLOCK DIAGRAM OF INSTRUMENTATION FOR IGNITION STUDIES
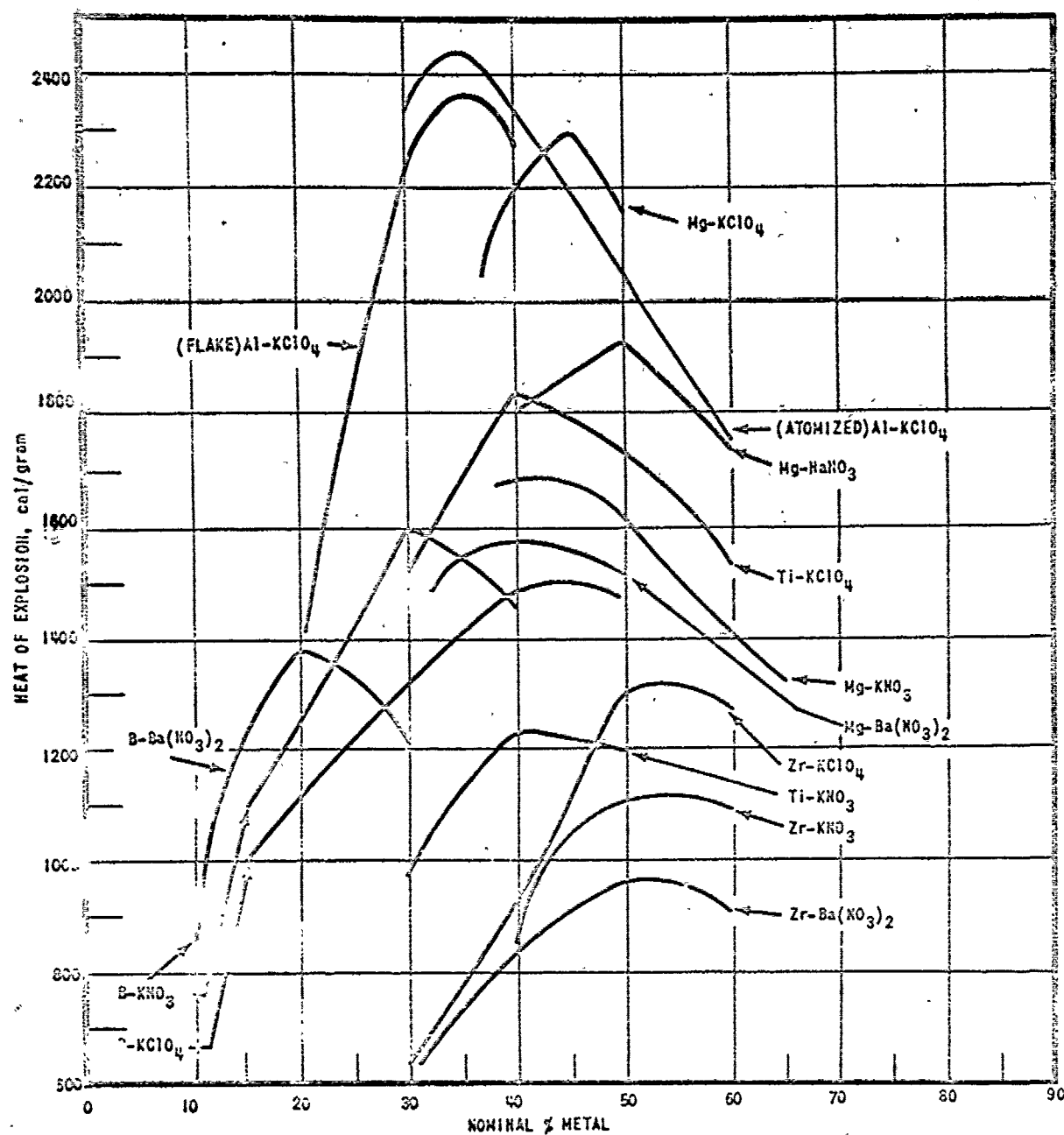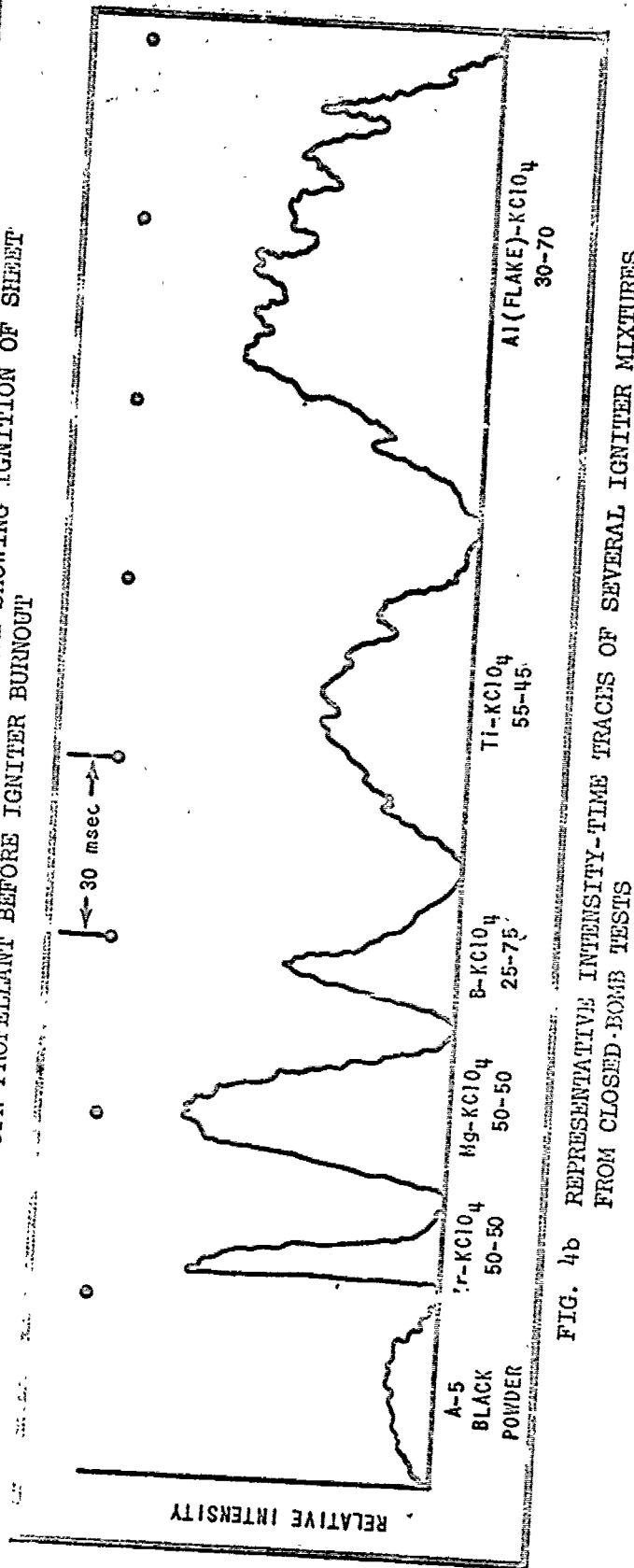
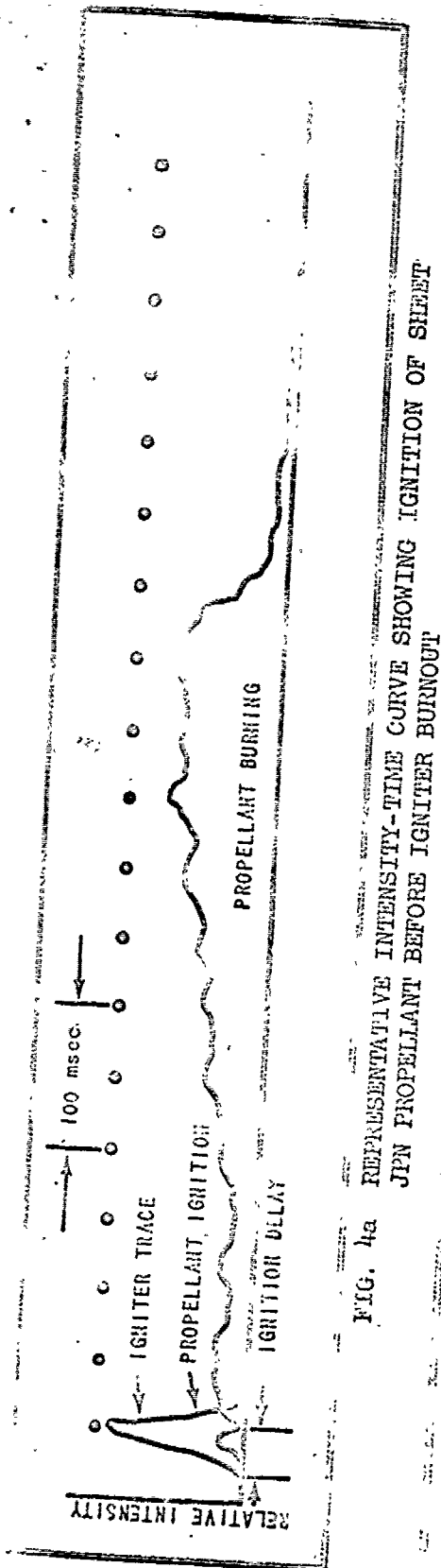FIG. 2b BLOCK DIAGRAM OF APPARATUS FOR IGNITION STUDIES

FIG. 3   MEASURED HEATS OF EXPLOSION OF METAL-OXIDANT MIXTURES

FIG. 4a REPRESENTATIVE INTENSITY-TIME CURVE SHOWING IGNITION OF SHEET
JPN PROPELLANT BEFORE IGNITER BURNOUT

FIG. 4b REPRESENTATIVE INTENSITY-TIME TRACES OF SEVERAL IGNITER MIXTURES
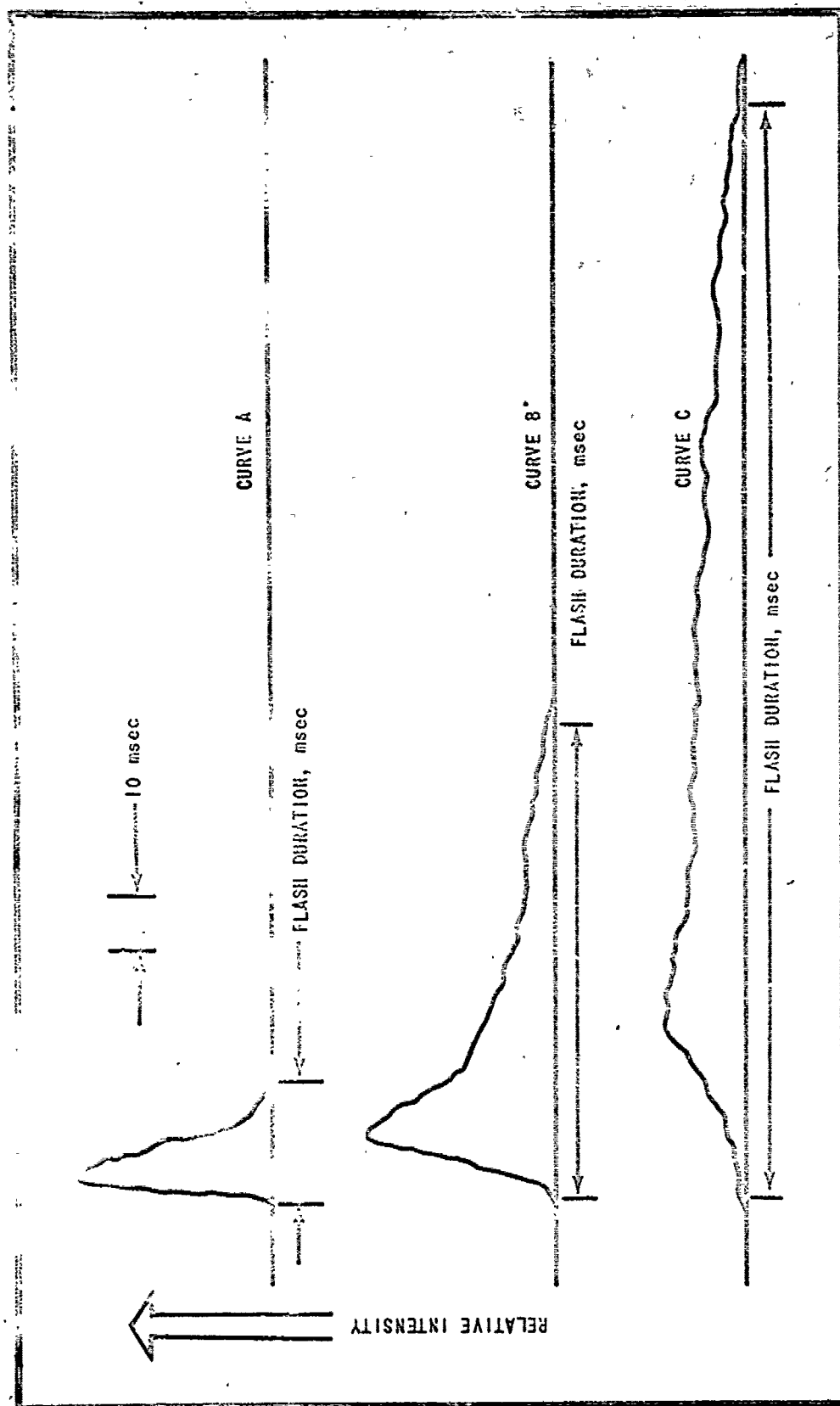FROM CLOSED-BOMB TESTS

FIG. 5 TYPICAL CURVES OF INTENSITY vs. TIME OBTAINED WITH BORON-POTASSIUM PERCHLORATE MIXTURES USING VARIOUS LOTS OF BORON